Practical and Highly Enantioselective Synthesis of β -Alkynyl- β -Amino Esters Through Ag-Catalyzed Asymmetric Mannich Reactions of Silylketene Acetals and Alkynyl Imines

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SUPPORTING INFORMATION PART 1

General. Infrared (IR) spectra were recorded on a Perkin Elmer 781 spectrophotometer, $\nu_{\max}$ in cm^{-1} . Bands are characterized as broad (br), strong (s), medium (m), or weak (w). ^1H NMR spectra are recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuteration as the internal standard (CDCl_3 : δ 7.26). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants in Hz. ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : δ 77.16). Enantiomeric ratios were determined by high-performance liquid chromatography (HPLC) on a Shimadzu chromatograph and chiralpak AD, OD and OJ columns (4.6 mm x 250 mm chiral column by Chiral Technologies) in comparison with authentic racemic materials. All high-resolution mass spectrometry were performed at Boston College on a Micromass LCT ESI-MS (positive mode). Optical rotation values were recorded on a Rudolph Research Analytical Autopol IV polarimeter.

Unless otherwise stated, all reactions conducted under open atmosphere in 13 x 100 mm borosilicate test tubes. J.T. Baker reagent grade THF was used without purification. Fisherbrand HPLC grade 2-Propanol was used without purification. Unless otherwise stated, silver acetate (99%), iodobenzene diacetate, $\text{Pd}(\text{C})$, phenylpropargyl aldehyde, succinic anhydride, 4-aminobenzamidine dihydrochloride, DMF, *p*-anisidine and *o*-anisidine were purchased from Aldrich and used without purification. Unless otherwise noted, EDC•HCl, HOBt•H₂O, Boc_2O , Cbz-Val-OSu were purchased from Advanced Chemtech and used without purification. All alkynyl imines,¹ silylketene acetal **3**² and ligand **1**³ were prepared according to previously reported procedures.

1) Journet, M.; Cai, D.; DiMechele, L. M.; Larson, R. D. *Tetrahedron Lett.* **1998**, 39, 6427–6428.

2) Colvin, E. W. *Silicon Reagents in Organic Synthesis*, Academic Press, Boston **1988**.

Representative procedure for Ag-catalyzed asymmetric Mannich reaction with silylketene acetals. Chiral phosphine **1** (10.0 mg, 20 μ mol) and AgOAc (3.3 mg, 20 μ mol) were weighed into a 13 x 100 mm test tube. The contents were dissolved in 0.5 mL of THF and allowed to stir for 5 min at 22 °C. Imine **2b** (94 mg, 0.4 mmol) was added immediately followed by 35 μ L *i*-PrOH (0.45 mmol). The test tube was capped with a septum, and allowed to stir in a cryocool bath at -60 °C for 5 min. At this point, silyl ketene acetal **3** (167 mg, 0.8 mmol) was added and the resulting mixture was allowed to stir at -60 °C for 16 h. The reaction was quenched upon addition of 0.40 mL of a saturated aqueous solution of NaHCO₃ at -60 °C before allowing to warm to room temperature with vigorous stirring for 10 min. The reaction mixture was then filtered through silica gel and subsequently washed with 1:1 hexanes:Et₂O (150 mL). The filtrate was concentrated and the resulting crude brown oil purified by silica gel chromatography (9:1 hexanes:Et₂O) to deliver 135 mg (0.36 mmol, 91% yield) of the desired product **4b** as a light yellow oil.

(+)-3-(2-Methoxy-phenylamino)-5-trimethylsilanyl-pent-4-ynoic acid phenyl ester (4a). Isolated as a light yellow oil. IR (neat, NaCl): 3395 (br), 2974 (w), 2369 (w), 1759 (s), 1602 (m), 1507 (s), 1457 (m), 1255 (s), 1224 (m), 1199 (m), 1161 (m), 1130 (m), 1029 (w), 846 (s), 746 (m), 683 (w). ¹H NMR (CDCl₃, 400 MHz): δ 7.35-7.30 (2H, m), 7.21-7.16 (1H, m), 7.05-7.02 (2H, m), 6.87-6.70 (4H, m), 4.71-4.65 (2H, m), 3.80 (3H, s), 3.06 (1H, dd, *J* = 15.0, 6.0), 2.96 (1H, dd, *J* = 15.0, 6.2), 0.09 (9H, s). ¹³C NMR (CDCl₃, 100 MHz): δ 169.0, 150.7, 147.8, 135.9, 129.5, 126.1, 121.7, 121.3, 118.4, 112.3, 110.0, 104.6, 88.5, 55.7, 43.5, 41.0, 0.07. HRMS (ES) Calcd for C₂₁H₂₅NO₃NaSi: 390.1488; Found: 390.1501 (M+Na). $[\alpha]_D^{20}$ = +50.5 ° (*c* = 0.867, CHCl₃) for a 92% ee sample.

Optical purity of **4a** was established by chiral HPLC analysis (OD column, 90/10 hexanes/*i*PrOH eluent, 1 mL/min, lamp setting of 230nm, R_t(major) = 9.45, R_t(minor) = 15.57).

(+)-3-(2-Methoxy-phenylamino)-5-phenyl-pent-4-ynoic acid phenyl ester (4b). Isolated as a light yellow oil. IR (neat, NaCl): 3389 (s), 1759 (s), 1602 (m), 1501 (s), 1457 (m), 1350 (m), 1249 (s), 1224 (s), 1186 (s), 1167 (s), 1123 (s), 1029 (m), 746 (s), 695 (s). ¹H NMR (CDCl₃, 400 MHz): δ 7.41-7.35 (4H, m), 7.31-7.22 (4H, m), 7.13-7.10 (2H, m), 6.95-6.92 (2H, m), 6.84-6.77 (2H, m), 5.00-4.95 (1H, bm), 4.86-4.84 (1H, bm), 3.86 (3H, s), 3.22 (1H, dd, *J* = 15.1, 6.8), 3.15 (1H, dd, *J* = 15.1, 6.6). ¹³C NMR (CDCl₃, 100 MHz): δ 169.1, 150.7, 147.8, 135.9, 131.9, 129.6, 128.5, 128.3, 126.1, 122.7, 121.7, 121.3, 118.4, 112.2, 110.0, 88.2, 83.7, 55.6, 43.3, 41.1. HRMS (ES) Calcd for C₂₄H₂₁NO₃Na: 394.1425; Found: 394.1419 (M+Na). $[\alpha]_D^{20}$ = +54.7 ° (*c* = 3.03, CHCl₃) for a 92% ee sample.

Optical purity of **4b** was established by chiral HPLC analysis (OD column, 92/8 hexanes/*i*PrOH eluent, 1 mL/min, lamp setting of 254 nmm, R_t(major) = 27.81, R_t(minor) = 30.64).

(+)-5-(4-Methoxy-phenyl)-3-(2-methoxy-phenylamino)-pent-4-ynoic acid phenyl ester (4c). The representative procedure described above was followed, except that reaction time was 36 h. **4c** was isolated as a light yellow oil. IR (neat, NaCl): 3389 (w), 2835 (w), 1759 (s), 1608 (s), 1513 (s), 1451 (m), 1249 (s), 1199 (m), 1167 (m), 1029 (m), 840 (m), 739 (m), 689 (m). ¹H NMR (CDCl₃, 400 MHz): δ 7.38-7.30 (4H, m), 7.25-7.20 (1H, m), 7.10-7.08 (2H, m), 6.93-6.90 (2H, m), 6.93-6.75 (4H, m), 4.95 (1H, dd, *J* = 6.8, 6.6), 4.83 (1H, bs), 3.85 (3H, s), 3.78 (3H, s), 3.20 (1H, dd, *J* = 15.0, 6.6), 3.12 (1H, dd, *J* = 15.0, 6.6). ¹³C NMR (CDCl₃, 100 MHz): δ 169.2, 159.7, 150.7, 147.7, 136.0, 133.3, 129.5, 126.1, 121.7, 121.3, 118.4, 114.8, 113.9, 112.2, 110.0, 86.7, 83.6, 55.6, 55.4, 43.3, 41.2. HRMS (ES) Calcd for C₂₅H₂₄NO₄: 402.1701; Found: 402.1705 (M+H⁺). [α]_D²⁰ = +52.8 ° (*c* = 2.00, CHCl₃) for a 92% ee sample.

Optical purity of **4c** was established by chiral HPLC analysis (OD column, 80/20 hexanes/ *i*-PrOH eluent, 1 mL/min, lamp setting of 254 nm, R_t(major) = 18.78, R_t(minor) = 27.70).

3-(2-Methoxy-phenylamino)-5-naphthalen-1-yl-pent-4-ynoic acid phenyl ester (4d). The representative procedure described above was followed, except that reaction time was 36 h. **4d** was isolated as a light yellow oil. IR (neat, NaCl): 3395 (w), 3055 (w), 1759 (s), 1513 (s), 1602 (s), 1457 (m), 1249 (s), 1218 (s), 1193 (s), 1161 (s), 1123 (s), 1029 (m), 802 (m), 777 (m), 739 (m), 689 (m). ¹H NMR (CDCl₃, 400 MHz): δ 8.14 (1H, d, *J* = 8.1), 7.81 (2H, dd, *J* = 7.3, 6.8), 7.62 (1H, d, *J* = 7.1), 7.51-7.35 (5H, m), 7.26-6.82 (7H, m), 5.13 (1H, dd, *J* = 6.4, 6.2), 5.00 (1H, bs), 3.87 (3H, s), 3.34 (1H, dd, *J* = 15.2, 6.4), 3.26 (1H, dd, *J* = 15.2, 6.4). ¹³C NMR (CDCl₃, 100 MHz): δ 169.4, 150.9, 148.2, 136.2, 133.6, 133.3, 130.8, 129.7, 129.1, 128.4, 127.1, 126.6, 126.5, 126.3, 125.4, 121.9, 121.5, 120.5, 118.9, 113.0, 110.3, 93.4, 82.0, 55.8, 43.9, 41.3. HRMS (ES) Calcd for C₂₈H₂₄NO₃: 422.1761; Found: 422.1756 (M+H⁺). [α]_D²⁰ = +63.2 ° (*c* = 1.13, CHCl₃) for a 92% ee sample.

Optical purity of **4d** was established by chiral HPLC analysis (OD column, 80/20 hexanes/ *i*-PrOH eluent, 1 mL/min, lamp setting of 254nm, R_t(major) = 28.66, R_t(minor) = 46.48).

(+)-3-(2-Methoxy-phenylamino)-undec-4-ynoic acid phenyl ester (4e). Isolated as a light yellow oil. IR (neat, NaCl): 2930 (s), 2860 (m), 1765 (s), 1608 (s), 1513 (s), 1457 (s), 1249 (s), 1230 (s), 1199 (s), 1161 (s), 1123 (s), 1035 (s), 739 (s), 689 (m). ¹H NMR (CDCl₃, 400 MHz): δ 7.37 (2H, dd, *J* = 8.1, 7.5), 7.22 (1H, dd, *J* = 8.6, 7.5), 7.08 (2H, dd, *J* = 7.5, 0.7), 6.92-6.73 (4H, m), 4.70 (2H, bs), 3.83 (3H, s), 3.10 (1H, dd, *J* = 0.1, 14.5), 3.00 (1H, dd, *J* = 0.1, 14.5), 2.16 (2H, dd, *J* = 7.0, 7.0), 1.49-1.20 (8H, m), 0.86 (3H, t, *J* = 6.6). ¹³C NMR (CDCl₃, 100 MHz): δ 169.2, 150.7, 147.7, 136.1, 129.5, 126.0, 121.7, 121.3, 118.1, 112.1, 110.0, 84.3, 79.0, 55.6, 42.8, 41.4, 31.5, 28.7, 28.5, 22.6, 18.8, 14.2. HRMS (ES) Calcd for C₂₄H₂₉NO₃Na: 402.2039; Found: 402.2045 (M+Na). [α]_D²⁰ = +26.5 ° (*c* = 1.57, CHCl₃) for an 86% ee sample.

Optical purity of **2e** was established by chiral HPLC analysis (OD column, 95/5 hexanes/*i*PrOH eluent, 1 mL/min, lamp setting of 254nm, R_t(minor) = 20.83, R_t(major) = 29.89).

(+)-3-(2-Methoxy-phenylamino)-6-methyl-6-trimethylsilanyloxy-hept-4-ynoic acid phenyl ester (4f). The representative procedure described above was followed, except that the crude product was purified by silica gel washed with 1% Et₃N and eluted with 99:1 hexane:Et₂O. **4f** was isolated as a light yellow oil. IR (neat, NaCl): 3376 (br), 2980 (m), 2363 (m), 1759 (s), 1602 (m), 1507 (s), 1451 (m), 1249 (s), 1161 (s), 1123 (m), 1035 (s), 840 (s), 739 (m), 683 (m). ¹H NMR (CDCl₃, 400 MHz): δ 7.39-7.33 (2H, m), 7.25-7.20 (1H, m), 7.09-7.07 (2H, m), 6.9-6.73 (4H, m), 4.78-4.69 (2H, m), 3.82 (3H, s), 3.09 (1H, dd, J = 6.2, 15.0), 3.02 (1H, dd, J = 6.2, 15.0), 1.42 (6H, d, J = 3.7), 0.1 (9H, s). ¹³C NMR (CDCl₃, 100 MHz): δ 169.0, 150.7, 147.8, 136.1, 129.6, 126.1, 126.0, 121.7, 121.3, 118.5, 112.4, 110.0, 88.7, 81.8, 66.6, 55.6, 42.9, 41.0, 33.2, 2.0. HRMS (ES) Calcd for C₂₄H₃₂NO₄Si: 426.2101; Found: 426.2101 (M+H⁺). $[\alpha]_D^{20}$ = +28.5 ° (c = 0.0135, CHCl₃) for an 84% ee sample.

The optical purity of **4f** was established by chiral HPLC analysis (OD column, 90/10 hexanes/ *i*-PrOH eluent, 1 mL/min, lamp setting of 230nm, R_t(major) = 9.75, R_t(minor) = 17.35).

(+)-5-Cyclohex-1-enyl-3-(2-methoxy-phenylamino)-pent-4-ynoic acid phenyl ester (4g). Isolated as a light yellow oil. IR (neat, NaCl): 3389 (br), 2942 (m), 2873 (w), 1759 (s), 1602 (s), 1513 (s), 1463 (s), 1249 (s), 1224 (s), 1199 (s), 1167 (s), 1123 (s), 1029 (m), 746 (m), 683 (m). ¹H NMR (CDCl₃, 400 MHz): δ 7.40-7.35 (2H, m), 7.25-7.20 (1H, m), 7.10-7.08 (2H, m), 6.92-6.73 (4H, m), 6.06 (1H, m), 4.84 (1H, dd, J = 6.6, 6.6), 4.75 (1H, bs), 3.83 (3H, s), 3.13 (1H, dd, J = 15.0, 6.6), 3.11 (1H, J = 15.0, 6.6), 2.07-2.05 (4H, m), 1.61-1.52 (4H, m). ¹³C NMR (CDCl₃, 100 MHz): δ 169.1, 150.7, 147.7, 136.0, 135.4, 129.5, 126.1, 121.7, 121.3, 120.2, 118.2, 112.1, 110.0, 85.5, 85.3, 55.6, 43.2, 41.3, 29.3, 25.7, 22.3, 21.2. HRMS (ES) Calcd for C₂₄H₂₆NO₃: 376.1919; Found: 376.1913 (M+H⁺). $[\alpha]_D^{20}$ = +25.7 ° (c = 2.57, CHCl₃) for a 90% ee sample.

Optical purity of **4g** was established by chiral HPLC analysis (OD column, 90/10 hexanes/ *i*PrOH eluent, 1 mL/min, lamp setting of 254nm, R_t(major) = 13.95, R_t(minor) = 20.00).

(+)-5-Cyclopropyl-3-(2-methoxy-phenylamino)-pent-4-ynoic acid phenyl ester (4h). Isolated as a light yellow oil. IR (neat, NaCl): 3389 (w), 2250 (w), 1759 (s), 1602 (m), 1513 (s), 1451 (m), 1243 (s), 1218 (s), 1193 (s), 1167 (s), 1123 (s), 1029 (m), 739 (s), 683 (m). ¹H NMR (CDCl₃, 400 MHz): δ 7.39-7.34 (2H, m), 7.24-7.20 (1H, m), 7.10-7.07 (2H, m), 6.91-6.72 (4H, m), 4.67 (2H, bs), 3.83 (3H, s), 3.07 (1H, dd, J = 14.8, 6.0), 2.96 (1H, dd, J = 15.0, 6.1), 1.26-1.18 (1H, m), 0.75-0.70 (2H, m), 0.64-0.60 (2H, m). ¹³C NMR (CDCl₃, 100 MHz): δ 169.2, 150.7, 147.6, 136.1, 129.5, 126.0, 121.7, 121.3, 118.1, 112.0, 110.0, 87.4, 74.1, 55.6, 42.8, 41.4, 8.3, 8.2. HRMS (ES) Calcd for C₂₁H₂₂NO₃: 336.1589; Found: 336.1586 (M+H⁺). $[\alpha]_D^{20}$ = +47.6 ° (c = 2.00, CHCl₃) for a 90% ee sample.

Optical purity of **4h** was established by chiral HPLC analysis (OD column, 90/10 hexanes/ *i*PrOH eluent, 1 mL/min, lamp setting of 220nm, R_t(minor) = 18.99, R_t(major) = 21.74).

(-)-3-(2-Methoxy-phenylamino)-5-naphthalen-1-yl-pentanoic acid phenyl ester (5). To a solution of **4d** (100 mg of a 92% ee sample, 0.24 mmol) in MeOH (15 mL) was added 50.5 mg Pd(C) (20 mol % Pd, 10% Pd(C)). The headspace of the solution was purged with H₂ and the mixture was allowed to stir at 23 °C under 1 atmosphere of H₂ (balloon) for 3 h after which time the solution was filtered through celite, which was subsequently washed with MeOH (3x10 mL). Removal of the volatiles and purification of the resulting residue by silica gel column chromatography (9:1 hexanes:Et₂O) provided 85 mg (0.20 mmol; 84% yield) of **5**. IR (neat, NaCl): 3412 (br), 2940 (w), 1752 (s), 1608 (m), 1510 (s), 1464 (m), 1250 (m), 1221 (s), 1193 (s), 1164 (m), 1123 (m), 1031 (m), 783 (m), 737 (s), 691 (w). ¹H NMR (CDCl₃, 400 MHz): δ 8.03 (1H, dd, *J* = 4.0, 2.9), 7.86 (1H, dd, *J* = 5.7, 4.0), 7.73 (1H, dd, *J* = 8.0, 8.0), 7.49-7.18 (7H, m), 6.91-6.71 (6H, m), 4.51 (1H, bs), 4.10 (1H, bs), 3.88 (3H, s), 3.39-3.19 (2H, m), 2.92 (1H, dd, *J* = 14.8, 5.7), 2.77 (1H, dd, *J* = 14.8, 5.7), 2.28-2.08 (2H, m). ¹³C NMR (CDCl₃, 100 MHz): δ 170.4, 150.6, 147.3, 137.8, 137.0, 134.1, 131.9, 129.5, 129.0, 127.0, 126.3, 126.1, 126.0, 125.7, 125.6, 123.8, 121.7, 121.6, 117.1, 110.9, 110.0, 55.6, 50.3, 40.1, 36.5, 29.7. HRMS (ES) Calcd for C₂₈H₂₈NO₃: 426.2076; Found: 426.2069 (M+H⁺). [α]_D²⁰ = -10.7 ° (*c* = 2.74, CHCl₃) for a 92% ee sample.

(+)-3-tert-Butoxycarbonylamino-5-phenyl-pent-4-ynoic acid phenyl ester (6). To a solution of PhI(OAc)₂ (0.70 g, 2.1 mmol) in MeOH (10 mL) and AcOH (0.5 mL) at 22 °C was added a solution of **4b** (0.20 g, 0.54 mmol) in MeOH (2 mL) slowly at 22 °C over 30 min. The mixture was then allowed to stir at 22 °C for an additional 30 min upon which time 5 mL of a 10% aqueous solution of HCl was added. The mixture was allowed to stir for 30 min at which time 5 mL of a 20% aqueous solution of Na₂S₂O₃ was added and stirring was allowed to continue for an additional 30 min. The solution was made basic by the addition of Na₂CO₃(s) (solution turned dark red) and Boc₂O (0.46 g, 2.1 mmol) was added followed by CH₂Cl₂ (5 mL). The mixture was allowed to stir at 22 °C for 12 h. The layers were separated and the aqueous layer was washed with CH₂Cl₂ (2 x 25 mL). The combined organic layers were washed with brine (1 x 10 mL), dried over MgSO₄ and volatiles were removed in vacuo. The desired product was recrystallized from hot hexanes to afford **6** (137 mg, 0.37 mmol, 68% yield) as a white solid. IR (neat, NaCl): 3345 (br), 2986 (w), 1759 (s), 1715 (s), 1495 (s), 1369 (m), 1193 (m), 1161 (s), 1023 (w), 765 (m), 689 (m). ¹H NMR (CDCl₃, 400 MHz): δ 7.43-7.08 (10H, m), 5.37 (1H, bs), 5.16 (1H, bs), 3.95 (1H, dd, *J* = 15.6, 5.5), 3.00 (1H, dd, *J* = 15.6, 5.6), 1.47 (9H, s). ¹³C NMR (CDCl₃, 100 MHz): δ 168.9, 154.8, 150.6, 131.9, 129.6, 128.7, 128.4, 126.2, 122.4, 121.7, 86.9, 83.8, 80.4, 41.1, 40.3, 28.5. HRMS (ES) Calcd for C₂₂H₂₃NO₄Na: 388.1524; Found: 388.1525 (M+Na⁺). [α]_D²⁰ = +45.6 ° (*c* = 1.64, CHCl₃) for a 92% ee sample.

(+)-3-(2-Benzyloxycarbonylamino-3-methylbutyrylamino)-5-phenylpent-4-ynoic acid tert-butyl ester (10). To a solution of PhI(OAc)₂ (0.50 g, 1.6 mmol) in MeOH (15 mL) and AcOH (0.1 mL) at 22 °C was added a solution of **4b** (0.13 g, 0.35 mmol) in MeOH (2 mL)

slowly at 22 °C over 30 min. The mixture was then allowed to stir at 22 °C for an additional 30 min upon which time 5 mL of a 10% aq. HCl solution was added. The mixture was allowed to stir for 30 minutes at which time 5 mL of a 20% aqueous solution of Na₂S₂O₃ was added and stirring was continued for an additional 30 min. The resulting mixture was made basic by the addition of Na₂CO₃(s) (solution turned dark red). Cbz-Val-OSu (0.85 g, 2.4 mmol) was added, followed by CH₂Cl₂ (5 mL). The mixture was allowed to stir at 22 °C for 12 h. The layers were then separated and the aqueous layer was washed with CH₂Cl₂ (2 x 25 mL). The combined organic layers were washed with brine (1 x 10 mL), dried over MgSO₄ and volatiles were removed in vacuo. The resulting residue was purified by silica gel chromatography (3:2 EtOAc:hexanes) to afford **10** (127 mg, 0.26 mmol, 73% yield) as a white solid. IR (neat, NaCl): 3307 (br), 2986 (w), 2980 (m), 1727 (s), 1526 (s), 1369 (m), 1249 (m), 1155 (s), 1029 (w), 752 (m), 689 (m). ¹H NMR (CDCl₃, 400 MHz): δ 7.37-7.24 (10H, m), 6.93 (1H, d, *J* = 8.6), 5.41 (1H, dd, *J* = 8.6, 9.1), 5.28-5.23 (1H, m), 5.10 (2H, s), 4.07-4.00 (1H, m), 2.73 (1H, dd, *J* = 15.8, 4.8), 2.61 (1H, dd, *J* = 15.8, 4.9), 2.17-2.10 (1H, m), 1.45 (9H, s), 0.99-0.90 (6H, m). ¹³C NMR (CDCl₃, 100 MHz): δ 170.1, 169.8, 169.7, 131.9, 131.8, 128.6, 128.5, 128.5, 128.3, 128.2, 128.2, 128.1, 128.1, 81.8, 81.7, 40.8, 38.7, 38.6, 28.2, 19.2, 19.1. HRMS (ES) Calcd for C₂₈H₃₄N₂O₅Na: 501.2365; Found: 501.2368 (M+Na). [α]_D²⁰ = +0.2 ° (*c* = 0.93, CHCl₃) for a >98% ee sample.